Estimated Stability of Perfluoroammonium Ion and its Salts

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Introduction

The hypothetical salt NF_4ClO_4 would clearly be an excellent oxidizing agent if it could be made. The object of the present paper is to present some estimates concerning the stability of the ion NF_4^+ and of its salts. Our first concern is to estimate the heat of formation of the perfluoroammonium ion in the gas phase.

A rough estimate can be made on the assumption that the dissociation energy of a fluorine atom from NF_4^+ is about the same as the average bond energy in NF_3^+. From the known heat of formation and ionization potential[a] of NF_3

(a) See thermochemical data assembled in appendix.

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we obtain

$$NF_3^+ = N^+ + 3F \qquad \Delta H = 119 \pm 6 = 3 \times (40 \pm 2) \text{ kcal/mole}$$

$$NF_4^+ = NF_3^+ + F \qquad \Delta H \approx 40 \text{ kcal/mole}$$

whence the heat of formation of NF_4^+ is about 255 kcal/mole.

An alternative estimate can be made by examining trends in the dissociation energy of a fluorine atom from the series of molecules CF_2, CF_3, CF_4, and the iso-electronic series NF_2^+, NF_3^+, (NF_4^+). The somewhat uncertain data (see appendix) are shown in the following table.

Dissociation Energy of Fluorine Atom from Various Species
kcal/mole

CF_2	CF_3	CF_4
133 ± 10	95 ± 7	122 ± 2
NF_2^+	NF_3^+	NF_4^+
74 ± 9	26 ± 6	?

The assumption of a parallel behavior in the two series leads to an estimate of for the dissociation energy of fluorine atom from NF_4^+ between perhaps 40 and 85 kcal/mole and a heat of formation for the ion of 208-253 kcal/mole.

A search has been made for the NF_4^+ ion as a possible product of the ion-molecule reaction

$$NF_3^+ + NF_3 = NF_4^+ + NF_2$$

in a mass spectrometer (Consolidated Model 21-103A). Observations were made at the partial pressure of 200 microns Hg of NF_3 in the sample reservoir, with the ionization chamber operating at 260°C and with 70 volt ionizing electrons.[a]

(a) These experiments were carried out by D. O. Schissler and P. A. Wadsworth of these laboratories, whose assistance is gratefully acknowledged.

No formation of NF_4^+ was observed though in an experiment with CD_4 under similar conditions the ion CD_5^+ was clearly detected. In a similar experiment with CD_4 and NF_3 each at 200 microns partial pressure, CD_5^+ and NF_3D^+ were clearly observed but no trace of NF_4^+ was found. If failure to find NF_4^+ is due to endothermicity of the reaction written above, then $\Delta H_f(NF_4^+)$ is not much less than 230 kcal/mole. Observation of the ion NF_3D^+ implies, on the other hand, $\Delta H_f(NF_3H^+) < 225$ kcal/mole. This corresponds to a dissociation energy $D(NF_3^+\text{-}H) > 100$ kcal/mole; the dissociation energy of H from the ions NH^+ to NH_4^+ is known to fall in the range 120-135 kcal/mole.

It seems then reasonable to conclude that the heat of formation of NF_4^+ is greater than 225 kcal/mole, and probably less than 260 kcal/mole. This implies that dissociation of NF_4^+ into NF_3^+ and F should be endothermic by 35 to 65 kcal/mole, and dissociation to $NF_2^+ + F_2$ endothermic by 15 to 60 kcal/mole. The increase of entropy in the latter dissociation is estimated about 45 e.u.; this will contribute -13.5 kcal/mole to the standard free energy of dissociation at 300°K and -24 kcal/mole at 260°C. Decomposition of $NF_4^+(g)$ into $NF_2^+(g)$ + $F_2(g)$ thus appears unlikely at 300°K but may be possible at moderately elevated temperatures and low pressures.

Let us turn now to the question of the lattice energy of salts of NF_4^+. For tetrahedral ions such as this one, the simplest approach, though an approximate one, is that proposed many years ago by Kaputinskii.[1] He assumed

(1) Kaputinskii, A., Z. Physik. Chem. B22, 257 (1933) and subsequent papers reviewed by him in Quart. Revs. 10, 284 (1956).

that for salts made up of combinations of spherical or tetrahedral ions the lattice energy could be well approximated by assigning to the crystal structure (usually unknown) a Madelung constant equal to that of sodium chloride and estimating the repulsive contribution to the lattice energy by a Born-Mayer expression similar to that which holds approximately for the alkali halides. These assumptions lead to the following expressions for the lattice energy U:

$$\begin{aligned} U &= Ne^2 \mu \frac{n}{2} \frac{\nu_+\nu_-}{R_+ + R_-} \left(1 - \frac{\rho}{R_+ + R_-}\right) \\ &= 290.2\, n \frac{\nu_+\nu_-}{R_+ + R_-} \left(1 - \frac{0.345}{R_+ + R_-}\right) \text{ kcal/formula wt.} \end{aligned} \qquad (1)$$

μ = Madelung constant = 1.7475 for NaCl
n = Number of ions per formula
ν = Ionic charge in units of electronic charge
R = Effective ionic radius
ρ = Born-Mayer repulsion parameter (exponential repulsive potential).

This expression has turned out to be remarkably useful for correlating the heats of formation of the salts of tetrahedral ions, provided suitable values are assumed for the "ionic radii" R_+ and R_-. It was recognized by Kapustinskii and his co-workers that these quantities are not necessarily equal to the packing radii of the ions in the actual structure of the crystal; as a consequence they have come to be known as thermochemical radii. The thermochemical radius and heat of formation for a tetrahedral ion are normally determined from equation (1) and the known heats of formation of two of its salts.

In order to apply (1) to the hypothetical salts of NF_4^+ it is necessary to estimate a thermochemical radius for that ion. We have found that a fairly good correlation exists for a number of symmetrical tetrahedral ions BX_4 between the thermochemical radius R_K and the sum of (a) the internuclear distance R(B-X) between the central atom of the ion and one of its ligands and (b) the van der Waals radius, $R_W(X)$ of the ligand. This correlation, shown in Figure 1, is described approximately by

$$R_K(BX_4^{-n}) = (0.75 \pm 0.07)\text{Å} + (0.55 \mp 0.024)(R(BX) + R_W(X)) \qquad (2)$$

with van der Waals radii 1.35 and 1.41 Å assigned to F and O respectively. The form of this correlation testifies to the artificial character of the thermochemical radii R_K.

The N-F distance in NF_3 is reported to be 1.37 Å[(2)]; the N-C distance

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(2) Interatomic Distances, L. E. Sutton, ed., The Chemical Society, London (1958)

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in the approximately tetrahedral complex $(CH_3)_3N{:}BF_3$ is reported as 1.50 Å, about 0.03 Å larger than in trimethylamine[(2)]. A recent x-ray crystallographic study of $(CH_3)_4N^+Br^-$ gave 1.50 ± 0.02 Å also as the N-C distance in the tetramethylammonium ion.[(3)] We therefore take the N-F distance in NF_4^+ as 1.40 Å.

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(3) Johnson, Q. C., USAEC, University of California Radiation Laboratory Report No. 9350 (1960).

From this and (2) we obtain a thermochemical radius of 2.26 Å for the perfluoroammonium ion.

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$NF_4^+F^-$: The lattice energy in this approximation is 147 kcal/mole (the Goldschmidt radius of 1.33 Å for fluoride ion was used in this computation since these radii were used by Kaputinskii). The recent photodetachment value for the electron affinity of fluorine[(4)] yields -60.7 kcal/mole for the heat

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(4) Berry, R. S. and Reimann, C. W., J. Chem. Phys. 38, 1540 (1963).

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of formation of $F^-(g)$. The calculated heat of formation of the hypothetical $NF_4^+F^-(c)$ is then 17 to 52 kcal/mole. This estimate is lowered only by

5 kcal/mole if the heat of formation of $F^-(g)$ is estimated from the heat of formation of KF(c) and the Kaputinskii formula. On the other hand, the standard heat of formation of $NF_3(g) + F_2(g)$ is -29.7 ± 1.8 kcal/mole; decomposition of the crystal should be exothermic by 50 to 80 kcal/mole.

$NF_4^+ClO_4^-$: The estimated lattice energy is 116 kcal/mole; a value of -88 kcal/mole is obtained for the heat of formation of ClO_4^- from the heat of formation of $KClO_4(c)$. The estimated heat of formation of $NF_4ClO_4(c)$ is then 21 to 56 kcal/mole. This is to be compared with about -30 kcal/mole for the heat of formation of $NF_3(g) + FClO_4(g)$.

$(NF_4)_2^+SO_4^=$: The Kaputinskii heat of formation of $SO_4^=$ estimated from the heat of formation of K_2SO_4 is -151 kcal/mole; the calculated lattice energy of $(NF_4)_2SO_4$ is 352 kcal/mole and its heat of formation thus -53 to +17 kcal/mole. For comparison the heat of formation of the possible decomposition products $2NF_3 + F_2O + SO_3$ is -146 kcal/mole. The heat of formation of $F_2SO_4(g)$, if it exists, is not known.

$NF_4^+BF_4^-$: The Kaputinskii heat of formation of $BF_4^-(g)$ estimated from the heat of formation of $KBF_4(c)$ (-454 kcal/mole) is -426 kcal/mole. The calculated lattice energy of $NF_4^+BF_4^-$ is 118 kcal/mole whence its heat of formation is -319 to -284 kcal/mole. This estimate is raised to -299 to -264 kcal/mole if the heat of formation of $BF_4^-(g)$ is taken to be -406 kcal/mole as estimated from a calculation of the Madelung energy of KBF_4.(5) It

(5) Waddington, T.C., "Lattice Energies", Advance in Inorganic Chemistry and Radiochemistry, Vol. 1, pp. 158-221, Academic Press, New York, 1959.

seems more appropriate, however, to use heats of formation estimated by the Kaputinskii approximation for use with that approximation.

The standard heat of formation of the possible dissociation products $NF_3 + F_2 + BF_3$ is 301 kcal/mole. The entropy of dissociation of the hypothetical crystal into these products is estimated to be about 120 e.u.. Thus, even if the heat of formation of $NF_4^+(g)$ is close to the estimated lower limit of 225 kcal/mole, crystalline NF_4BF_4 should be unstable relative to its decomposition products at temperatures about 150°K. It is possible, however, that the heat of formation of NF_4^+ is above 245 kcal/mole, in which case NF_4BF_4 may not be stable at any temperature.

Conclusion: Despite the uncertainties inherent in the Kaputinskii approximation and in the estimated heat of formation of $NF_4^+(g)$, it seems safe to conclude that the hypothetical salts NF_4F, NF_4ClO_4 and $(NF_4)_2SO_4$ are unstable relative to their possible decomposition products. The compound NF_4BF_4 may possibly be capable of existence at low temperatures; its estimated stability is marginal.

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APPENDIX

Thermochemical Data

Table 1.

Bond Dissociation Energies D, kcal/mole

Bond	D	Refs. and Notes
NF_2-F	56 ± 3.5	1, 2
NF-F, N-F	Av. 70.4 ± 1	1, 2
NF-F	69 ± 16	3
NF_2^+-F	26 ± 6	4
	23 ± 11	5
NF^+-F	74 ± 9	6
CF_3-F	122 ± 2	7
CF_3-H	102 ± 2	7
CF_2-F	~ 110	8
	95 ± 7	9
CF-F	~ 120	8
	133 ± 2	9
CF_2-CF_2	< 112	10

Table 2.

Enthalpies of Formation (300°K), kcal/mole

Substance	$\Delta H^\circ f$(a)	Reference
NF_3	-29.7 ± 1.8	11
NF_2	8.9 ± 1.7	2
CF_4	-218 ± 1	12-15
CF_3	-116 ± 5	7
C_2F_4	-151.8 ± 1	12,16
CF_2^+	247 ± 2	17
	249	18
CF_2	-30 ± 10	19,20
	-26 ± ?	21
	$<$ -20	22
	$>$ -39 ± 2	17
	-39	23
CF	74.7	20
BF_3	-271.2 ± 0.5	24
	-270.1 ± 0.5	25

Table 3.

Ionization Potentials, e. v.

Substance	I_z	Ref.
NF_3	13.20 ± 0.2	4
NF_2	11.8 ± 0.1	1,6
CF_2	$\leq$ 12.4	17

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2) Kennedy, A. and Colburn, C. B., J. Chem. Phys. 35, 1892 (1961).
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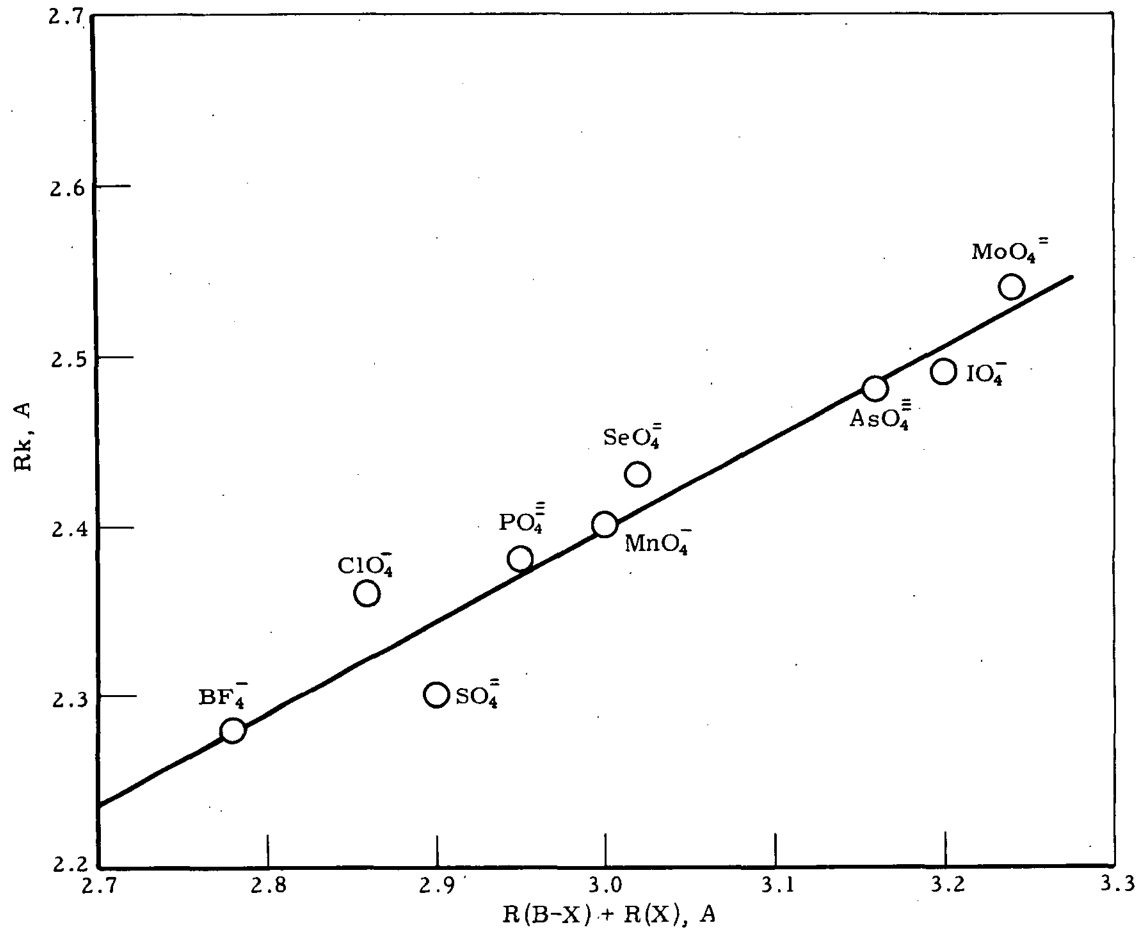

Figure 1. CORRELATION OF THERMOCHEMICAL RADIUS Rk WITH SUM OF BOND DISTANCE R(B-X) AND VAN DER WAALS RADIUS R(X) IN TETRAHEDRAL IONS